

EXTRACTION OF LOW-RANK COALS WITH SUPERCRITICAL WATER

M.L. Swanson, E.S. Olson, J.W. Diehl, and S.A. Farnum

University of North Dakota Energy Research Center
Box 8213, University Station
Grand Forks, ND 58202

Abstract

Supercritical water extractions were performed on low-rank coals utilizing a semicontinuous supercritical solvent extraction system. Percent conversions ranged from 40% to 50% while extract yields ranged from 10% to 30% at 380°C. The conversions and extract yields increased with increasing operating temperature and pressure. The conversions also decreased with increasing coal rank and correlated well with the percent volatile matter in the coals.

Organic analyses of the resulting extracts have included separations into pentane, methylene chloride and methanol soluble fractions by short column chromatography, 200 MHz proton NMR, IR spectroscopy and capillary gas chromatography. Proximate and ultimate analyses indicated that supercritical water extracts the volatile, hydrogen-rich fraction of the coal. Organic analyses show that the extract is highly polar in nature with significant quantities of phenols and long-chain aliphatic fatty acids.

Introduction

Interest in the extraction of solutes with supercritical solvents has been increasing rapidly over the past fifteen years. This interest is primarily due to the enhanced solubility of substrates in the fluid phase that occurs at or above the critical point. It has only been in the last few years that considerable research has addressed the use of supercritical water as a solvent suitable for obtaining high yields of environmentally acceptable fuels and chemical feedstocks from coal (1, 2, 3). Under ambient conditions, organics and water are generally immiscible. However, as water approaches its critical point, the solubility of organics in water increases drastically (4, 5) while the solubility of inorganics in water substantially decreases (6). These solubility changes contribute to the potential of supercritical water to obtain high yields of relatively ash-free hydrocarbons from coal. In addition, other investigations have shown the potential for increasing supercritical water yields even further through the addition of a reducing agent such as CO or H₂S to the supercritical water system (7, 8, 9).

The objective of this research was to investigate the use of water as a cheap supercritical extraction solvent for obtaining environmentally acceptable liquid fuels and chemical feedstocks from coal and attempt to use supercritical solvent extraction as a means for determining the composition of various molecular fractions present in low-rank coals.

Experimental Procedure

Supercritical water extractions were performed using a semicontinuous extraction system in which deionized water under supercritical conditions was passed through a fixed bed of coal. The coals used in this experiments included the Indian Head, Center, and Martin Lake lignites along with Sarpy Creek and Wyodak subbituminous coals. Proximate and ultimate analyses for these coals are shown in Table I. As shown in Table I, there was a difference between the beginning and ending samples of the Indian Head lignite used in these experiments. Figure 1 is a flowsheet of the supercritical solvent extraction system as it was used for most of the supercritical water experiments. In this system, a fixed bed of coal was detained by sintered metal frits in a horizontal section of high pressure tubing. A rehabilitated GC

TABLE I. Proximate and Ultimate Analyses of Coals Used in Supercritical Water Experiments

	Sample Name and Location					
	Indian Head 1 ND	Indian Head 2 Mercer Co., ND	Center Oliver Co., ND	Martin Lake Panola Co., TX	Wyodak Campbell Co., WY	Samy Creek Big Horn Co., MT
<u>Proximate Analysis (wt%)</u>						
Volatile Matter	43.8	49.8	43.0	42.2	43.5	34.8
Fixed Carbon	48.0	41.9	48.6	42.8	50.0	45.4
Ash	8.2	8.3	8.4	15.0	6.5	19.8
<u>Ultimate Analysis (wt%)</u>						
Hydrogen	4.74	4.45	4.13	0.32	4.26	3.64
Carbon	66.20	64.96	64.07	61.88	64.62	59.43
Nitrogen	0.96	1.00	1.13	1.23	1.01	0.83
Sulfur	0.72	0.33	1.16	1.17	0.58	4.22
Oxygen (1nd)	19.19	20.96	21.08	20.40	23.04	12.11
Ash	8.2	8.3	8.42	15.0	6.5	19.8

oven was used to heat the solvent and extraction vessel to temperature at 20°C/min., after which a pulseless flow of solvent was started through the system. The extracted organics and solvent then passed through a back pressure regulator where the precipitated extract was collected in a heated sample cylinder while the vaporous solvent and light gases were collected in chilled sample vessels. The volume of noncondensable product gas was measured and collected for analysis.

Analytical Procedure

After each experiment, any water remaining in the extract sample cylinder was filtered from the solid extract and selected samples of the recovered water solvent were analyzed by gas chromatography for their concentrations of water soluble organics. The solid extract was washed from the sample cylinder with acetone and the extracted coal residue and solvent-extract mixture were then rotary vacuum distilled to remove the solvent. This procedure allowed a relatively moisture-free product to be obtained for material balance purposes. Residues were analyzed by thermogravimetric analysis (TGA) and proximate and ultimate analyses were performed on selected samples.

Discussion and Results

The operating conditions and the corresponding results of these supercritical water extractions are shown in Tables II and III. The effect of extraction time on percent conversions is shown in Figure 2. This figure indicates that the percent conversions increase linearly with an increase in coal residence time up to approximately 45 minutes after which the conversions leveled off at 42% to 43%. A vacuum dried sample (0.65 wt% moisture) was also extracted for 60 minutes with supercritical water at similar operating conditions and resulted in a 33.5% conversion. This lower conversion was due to a sample size effect since drying the coal resulted in a 60% larger sample of maf coal being extracted. A conversion of 44.2% was obtained for a separate run using a vacuum dried coal at longer residence times which indicated that no advantage resulted in extracting "as received" coals with their inherent moisture already present in the sample's porous structure. Also, considering that a 33% larger sample of maf coal was being extracted, the slightly higher conversions obtained for the supercritical water experiment performed at a flow rate of 240 cc/hr suggests that an increase in the solvent flow rate increased the rate of extraction.

The effects of operating temperature and pressure on the resulting conversions was investigated using operating temperatures of 380°C or 440°C ($T_r = 1.01$ or 1.10) while the operating pressures used were 3265, 4013, or 4815 psia ($P_r = 1.02, 1.25, 1.50$). Results of these experiments are summarized in Table II. Figure 3 is a plot of the reduced pressure versus the percent conversion at both operating temperatures. This figure indicates that a small increase in the conversions was obtained with an increase in the operating temperature. The conversion also displayed a larger increase with increasing pressure up to 4000 psia. Above 4000 psia, there appeared to be no effect on the resulting conversions. This increase in conversions is the result of a large increase in solvent density caused by the increased pressure. The increase in conversion with higher temperature was the result increasing thermal decomposition or reactions of the lignite in this temperature region. The product gas compositions and yields appeared to be only temperature and coal dependent and were not affected to any large degree by operating pressure or solvent flow rate.

Table III shows the effect coal rank had on the percent conversion obtained using supercritical water at 380°C and pressures of either 3265 or 4013 psia. For comparison purposes, supercritical water experiments were also performed on a Red Lake Peat and a biomass sample and the results are also displayed in Table III. These results suggest that there is a high degree of correlation between the percent conversions obtained using supercritical water and the amount of volatile matter present in the starting coal. This finding is consistent with results reported by Great Britain's National Coal Board in which percent conversions using supercritical

TABLE II. Operating Conditions and Results from Supercritical Water Extractions of Indian Head Lignite

Coal	Temp (°C)	Tr**	Pressure (psia)	Pr**	Solvent Density (g/cc)	Solvent Flowrate (g/cc)	Residence Time (min)	Percent Conversion (MAF)	Extract Yield* (MAF)	Volatile Yield* (MAF)	Product Gas Yield*
Indian Head (as received)	380	1.009	3265	1.017	.193	120	15	25.2	8.0	0.2	5.5
Indian Head (as received)	380	1.009	3265	1.017	.193	120	30	34.3	10.4	1.4	10.4
Indian Head (as received)	380	1.009	3265	1.017	.193	120	45	43.1	10.1	2.2	9.6
Indian Head (as received)	380	1.009	3265	1.017	.193	120	60	42.7	22.6	ND	12.5
Indian Head (vacuum dried)	380	1.009	3265	1.017	.193	120	60	33.5	8.5	1.8	11.4
Indian Head (as received)	380	1.009	3265	1.017	.193	120	80	42.6	12.0	2.9	11.6
Indian Head (as received)	380	1.009	3265	1.017	.193	240	30	36.0	9.9	2.1	8.0
* Indian Head (as received)	380	1.009	3265	1.017	.193	120	240	43.3	18.8	2.5	10.8
* Indian Head (as received)	380	1.009	4013	1.250	.504	120	240	50.6	22.4	2.3	12.6
* Indian Head (as received)	380	1.009	4815	1.500	.558	120	240	50.3	23.8	2.9	12.1
Indian Head (as received)	440	1.102	3265	1.017	.097	120	240	43.3	13.3	ND	19.3
* Indian Head (as received)	440	1.102	4013	1.250	.137	120	240	53.2	21.1	ND	17.0
Indian Head (as received)	440	1.102	4815	1.500	.199	120	240	54.4	21.8	ND	16.3
Indian Head (vacuum dried)	380	1.009	3265	1.017	.193	120	150	44.2	12.2	2.3	16.7

* % conversion = $\frac{\text{wt maf coal} - \text{wt maf residue}}{\text{wt maf coal}}$; % yield = $\frac{\text{wt maf product}}{\text{wt maf coal}}$

+ - average value
ND - not determined

** Tr = operating temperature of solvent (°K); Pr = operating pressure of solvent (psia)
critical temperature of solvent (°K); critical pressure of solvent (psia)

TABLE III. Operating Conditions and Results from Supercritical Water Extractions of Low-Rank Coals

Coal	Temp (°C)	Tr**	Pressure (psia)	Pr**	Solvent Density (g/cc)	Solvent Flowrate (g/cc)	Residence Time (min)	Percent Conversion (MAF)	Extract Yield* (MAF)	Volatile Yield* (MAF)	Product Gas Yield*
Coal Type Experiments											
Center	380	1.009	3265	1.017	.193	120	60	43.4	24.6	ND	ND
Martin Lake	380	1.009	4013	1.250	.504	120	150	45.2	20.2	1.7	12.1
Wyodak	380	1.009	3265	1.017	.193	120	150	33.7	14.0	ND	14.5
Wyodak	380	1.009	4013	1.250	.504	120	150	39.5	15.0	1.6	22.4
Sarpy Creek	380	1.009	4013	1.250	.504	120	150	33.5	21.2	1.3	3.6
Red Lake Peat	380	1.009	3265	1.017	.193	120	60	75.8	25.6	3.6	20.5
Blomass (Douglas Fir Sawdust)	380	1.009	3265	1.017	.193	120	60	83.8	33.7	3.6	33.6
Lithotype Experiments											
Indian Head W train (50% of original)	380	1.009	3265	1.017	.193	120	60	42.3	22.2	6.9	6.7
Indian Head Durain (45% of original)	380	1.009	3265	1.017	.193	120	60	39.8	18.0	1.8	7.6
Indian Head Fusain (5% of original)	380	1.009	3265	1.017	.193	120	60	32.3	28.1	0.4	4.7
Special Run											
Indian Head (w 90% H ₂ O-10% CO)	383	1.003	3300	ND	ND	120+CO	60	41.2	12.3	2.1	NA

* % conversion = $\frac{\text{wt maf coal} - \text{wt maf residue}}{\text{wt maf coal}}$; % yield = $\frac{\text{wt maf product}}{\text{wt maf coal}}$

+ - average value
ND - not determined

** Tr = operating temperature of solvent (°C);
critical temperature of solvent (°K);

Pr = operating pressure of solvent (psia);
critical pressure of solvent (psia)

toluene also correlated well with volatile matter of the original coal (10). As a result, the conversions decreased with an increase in coal rank. This increase in conversions which occurred is the result of the increased concentration of thermally labile carbohydrate, lignin or lignin-derived components which exist in the lignite, peat, and biomass.

Supercritical water extractions of the Indian Head lithotypes; vitrain, durain, and fusain were performed. Approximately 12 to 15 grams of each lithotype were microscopically separated. The conversions obtained for the vitrain and durain fractions (which make up approximately 50 and 45 wt% of the original Indian Head) were found to be similar to those obtained using the original Indian Head lignite as shown in Table III. Table III also shows that the conversion of the fusain portion (5% of the original Indian Head) was significantly less than that for the original lignite. These results agree with other reported results in which vitrains and durains have been found to be highly susceptible to liquefaction, (i.e., susceptible to thermal cleavage and reaction with hydrogen) while fusain has been found to behave as more of an inert material (11). The yields of water-soluble organics from these lithotypes and the original lignite are shown in Table IV. As shown, the vitrain fraction contains considerably more of the oxygenated water-soluble volatile compounds (i.e., acetone, methanol, and phenol) than the original Indian Head, while the durain fraction contains slightly less of these compounds than the original lignite. The concentrations of these compounds in the fusain fraction were very small compared to that of the original lignite.

TABLE IV. Percent Yields of Volatile Components Found in Recovered Supercritical Water Solvent

Component	Supercritical Water Extraction				
	Indian Head 2	Sarpy Creek	Indian Head Vitrain	Indian Head Durain	Indian Head Fusain
Phenol	0.63	0.21	1.14	0.48	0.14
o-Cresol	0.17	0.06	0.20	0.10	0.05
m,p-Cresol	0.17	0.13	0.22	0.18	0.05
Total Phenolics	0.97	0.40	1.56	0.76	0.24
Methanol	0.80	0.04	1.32	0.22	--
Acetone	0.91	0.42	3.93	0.70	0.15
MEK	0.25	0.10	0.12	0.14	0.05
Total	2.93	0.96	6.93	1.82	0.44

As shown in Table III, a special experiment was performed using a 90-10 mole% mixture of water-carbon monoxide to extract Indian Head lignite at 383°C and 3300 psia. The purpose of this experiment was to determine what effects the addition of a reducing gas such as CO has on the molecular composition of the extract. The conversion and yields obtained were similar to those obtained for an experiment using pure water under similar conditions.

Results From Analysis of Supercritical Water Residues and Extracts

Proximate and ultimate analyses of selected residues and extracts from supercritical water and the original Indian Head are shown in Table V. The proximate analysis indicates that the supercritical water extract contains a significantly higher fraction of volatile matter while the residue contains a significantly lower fraction of volatile matter than the original Indian Head. The

TABLE V. Comparison of Proximate and Ultimate Analyses of Supercritical Water Residues and Extracts to the Original Sample

Sample Description - All Samples run at 380°C, 3265 psia, 120 cc/hr												
	Indian Head		Indian Head		Indian Head		Original		Red Lake Peat		Biomass	
	Water - 30 min	Residue Extract	Water - 60 min	Residue Extract	Water - 60 min	Residue Extract	Red Lake Peat	Residue Extract	Water - 60 min	Residue Extract	Water - 60 min	Residue Extract
Percent Conversion (MAF)	34.3		42.7		41.2		NA		74.7		NA	
Percent Extract Yield (MAF)	10.4		22.6		12.3		NA		26.1		NA	
Proximate Analysis (MF)												
Volatlie Matter	27.8	71.3	30.4	79.8	27.6	99.6	67.4	23.6	97.9	85.4	35.2	97.5
Fixed Carbon	63.8	26.7	61.0	19.8	60.7	0.4	12.9	32.8	1.9	13.2	62.0	2.5
Ash	8.4	2.0	8.6	0.4	11.7	0.0	19.7	43.6	0.2	1.4	2.8	0.0
Ultimate Analysis (MF)												
Hydrogen	3.67	7.67	3.53	7.63	3.41	9.01	2.62	2.52	8.51	6.55	3.62	6.28
Carbon	73.81	78.10	75.10	78.73	72.55	66.44	54.99	44.98	74.66	52.48	77.92	72.09
Nitrogen	1.34	0.69	1.38	0.84	1.40	0.72	2.89	2.22	2.80	0.40	0.75	0.71
Sulfur	0.42	1.42	0.38	0.42	0.39	0.30	0.31	0.25	0.15	0.09	0.13	0.08
Oxygen (Ind.)	12.36	10.11	11.01	11.97	10.54	23.53	19.49	6.43	13.67	39.09	14.78	20.84
Ash	8.4	2.0	8.6	0.4	11.7	0.0	19.7	43.6	0.2	1.4	2.8	0.0

ultimate analysis shows that the extract had a lower C/H ratio than the original Indian Head whereas the residue had a higher C/H ratio than the original Indian Head. These analyses indicate that the hydrogen-rich, lower molecular weight portion of the lignite is being extracted while leaving a highly carbonaceous residue.

The analyses also indicate that the mineral matter is concentrated in the residue while a relatively ash-free extract is obtained. Table V compares the proximate and ultimate analyses of the residues and extracts for runs using supercritical water and the supercritical water-CO mixture. The C/H ratio is substantially lower for the run using the H₂O-CO mixture which suggests the possible addition of H₂, which was generated by the water-gas shift reaction, to the extract.

Thermogravimetric analyses were performed in argon on samples of the original coal and supercritical water residues using a heating rate of 20°C/min. and a final temperature of 900°C. The weight-temperature profiles indicated that ~20 wt% of the supercritical residues were volatilized while approximately 41% of the original coal would volatilize under the same conditions. The differential weight loss curves for two supercritical water residues and the original Indian Head lignite are shown in Figure 4. This figure indicates that supercritical water has extracted most of the compounds which would devolatilize below ~550°C, thus, concentrating the higher molecular weight material in the residue which results in the higher differential weight loss curve at temperatures above 550°C.

Analysis of a supercritical water extract was carried out using chromatographic separations, infrared (IR), and nuclear magnetic resonance (NMR) spectroscopy. The extract was separated into three fractions by short column chromatography on silica gel. The first fraction was separated by successive elution with pentane and then isooctane. This fraction was found to make up approximately 5% of the extract and the NMR spectra showed that this fraction consisted only of aliphatic materials. This fraction was analyzed by capillary column gas chromatography and was found to contain a series of alkanes and alkenes in the range of C-18 to C-34. The presence of the alkenes indicates that thermal cracking is occurring but the relative amounts of the alkanes alternate as the carbon chain increases in the series, which suggest that the cracking was minimal, perhaps confined to reactions near the acid or ester function. Also, the predominance of the odd-number chains and the high concentration of CO₂ in the product gas indicate that a significant amount of decarboxylation was occurring.

The second fraction was separated by elution with methylene chloride and was found to make approximately 26% of the extract. Some identified individual hydrocarbons include phenanthrene, fluorene, anthracene, pyrene, benzofluorenes, and fluoranthene. The NMR spectrum shown in Figure 5 also suggests the possible presence of ester groups between 3.8 and 4.0 ppm. The last fraction was obtained by elution with methanol and was found to make up the majority (~69-70%) of the extract. The NMR and IR spectra on this fraction indicate the presence of phenolics and long chain aliphatic acids.

Table VI shows some of the individual coal-derived compounds which have been identified and their approximate yields. These yields indicate that the identified phenolics constituted a small fraction (from ~2.9% to 0.8%) of the supercritical water extracts. The dependence of phenol yields in the extract on coal type is noticeable with the Wyodak subbituminous coal generally yielding higher concentrations of phenols in the extract. The distribution of the individual phenols is essentially identical for the three coals, indicating that they originate from the same type of substructure in the coal and that the reactions which release them during supercritical water extraction must be identical. Thus, the ratio of the phenol yields in the three coals must result from different amounts of the substructure in the coals (probably in the same ratio).

TABLE VI. Identification and Determination of Yields for Individual Compounds in Supercritical Water Extracts Obtained at 380°C and 4013 psia

Compound	Indian Head % Yields (mcf)		Wyodak % Yields (mcf)		Martin Lake % Yield (mcf)	
	In	In	In	In	In	In
	Extract	Water	Extract	Water	Extract	Water
Methanol	ND	0.649	ND	0.113	ND	0.421
Acetone	ND	0.607	ND	0.538	ND	0.568
Acetonitrile	ND	0.001	ND	0.001	ND	0.005
Methyl Ethyl Ketone	ND	0.160	ND	0.170	ND	0.176
Propionitrile	ND	0.034	ND	0.005	ND	0.020
Catechol	ND	0.202	ND	0.151	ND	0.157
Phenol	0.028	0.362	0.075	0.340	0.026	0.167
o-cresol	0.022	0.101	0.062	0.104	0.020	0.049
m-cresol	0.030	0.110	0.067	0.094	0.024	0.049
p-cresol	0.030	0.118	0.007	0.122	0.022	0.059
2,6-diMePhe	0.002	ND	0.034	ND	+	ND
2-EtPhe	0.002	ND	0.045	ND	0.010	ND
2,4-diMePhe	0.013	ND	0.045	ND	0.017	ND
2,5-diMePhe	0.019	ND	0.018	ND	0.006	ND
2,3-diMePhe	0.009	ND	0.018	ND	0.006	ND
4-McGuaigcol	0.010	ND	0.003	ND	0	ND
2,4,6-triMePhe	0.007	ND	0 +	ND	+	ND
2,3,6-triMePhe	0.001	ND	0.003	ND	0	ND
2,4,5-triMePhe	0.004	ND	0.006	ND	0.020	ND
4-Indanol	+	ND	0.007	ND	0	ND
5-Indanol	0.009	ND	0.012	ND	0.012	ND
2,3,5,6-tetraMePhe	0.001	ND	0.003	ND	+	ND
1-Napthol	0.002	ND	0.006	ND	+	ND
2-Napthol	0.009	ND	0.018	ND	0.012	ND
Total	0.198	2.343	0.426	1.638	0.155	1.670

+ - trace

ND - not detected

References

1. Kershaw, J.R. and L.J. Bagnell. American Chemical Society, Div. Fuel Chem. Preprints; 1985, 30 (3), 101.
2. Scarrah, W.P. "Chemical Engineering at Supercritical Fluid Conditions," (M.E. Paulaitis, J.M.L. Penninger, R.D. Gray and P. Davidson, Eds.) Ann Arbor Science, Ann Arbor, 1983, pp. 385-407.
3. Deshpande, G.V., G.P. Holder, A.A. Bishop, J. Gopal, and I. Wender. Fuel, 1984, 63, p. 956.
4. Connolly, J.F., Journal of Chemical and Engineering Data, 1966 11 (1), pp. 13-16.
5. Wilson, G.M. and C. Tsonopoulos, AIChE Journal, 1983, 29 (6), pp. 990-999.
6. Gosephson, J. Environmental Science Technology. 1982, 16 (10), pp. 548A-551A.
7. Ross, D.S., G.P. Hum, T.C. Min, J.K. Green, and R. Mansoni. American Chemical Society, Div. Fuel Chem. Preprints, 1985, 30 (3), 94.
8. Ross, D.S. in "Coal Science 3, (M. Gorbaty, J. Larsen, and I. Wender, eds.) New York, 1984, pp. 301-338.
9. Stenberg, V.I., and J. Nowale, Proceedings of the 1985 International Conference on Coal Science, 1985, Pergamon Press, Sydney, Australia, pp. 103-105.
10. Whitehead, J.C., and Williams, D.F., Jour. Instit. Fuel, December 1975, p 182-184.
11. Berkowitz, N. "An Introduction to Coal Technology," Academic Press, New York, 1979, p. 112.

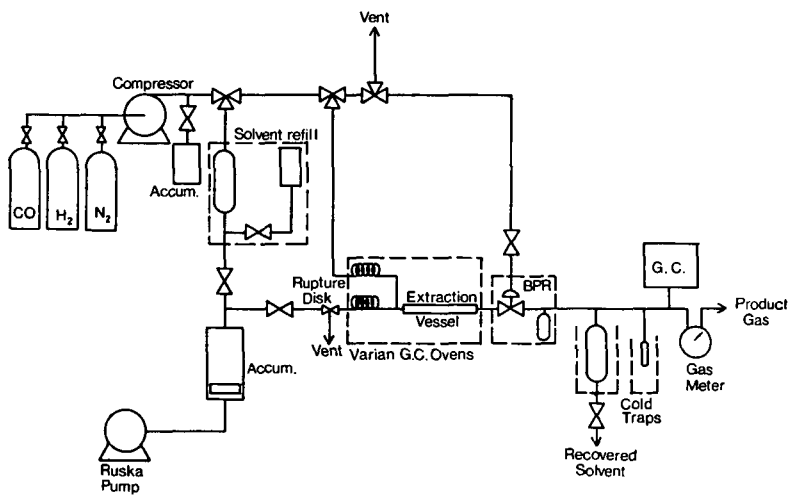


Figure 1. Flowsheet for the semicontinuous supercritical solvent extraction.

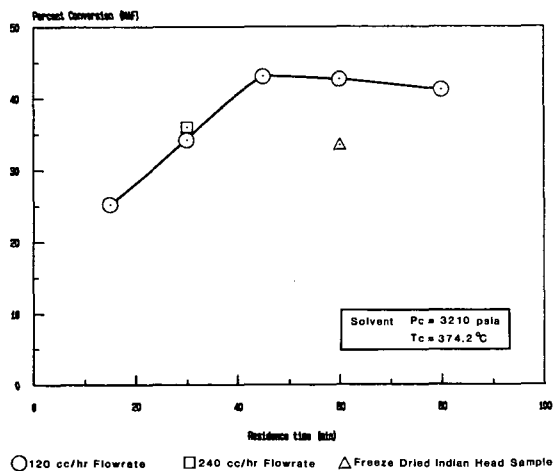


Figure 2. Extraction time and flow rate effects on supercritical water extraction.

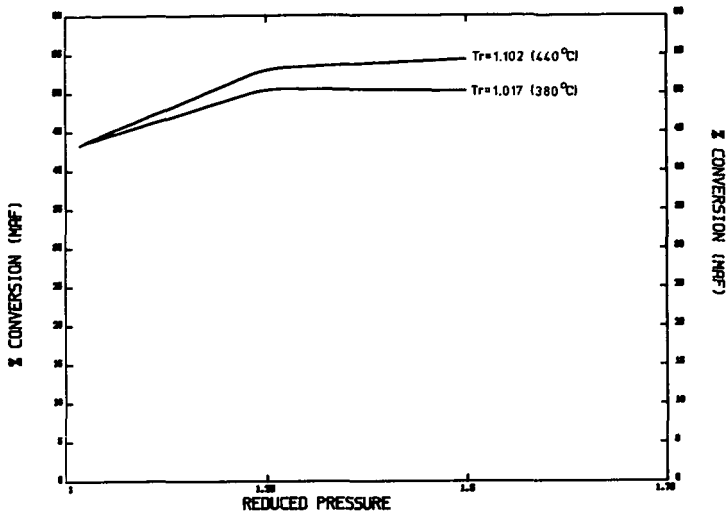


Figure 3. Effect of operating pressure and temperature on conversion of Indian Head lignite with supercritical water.

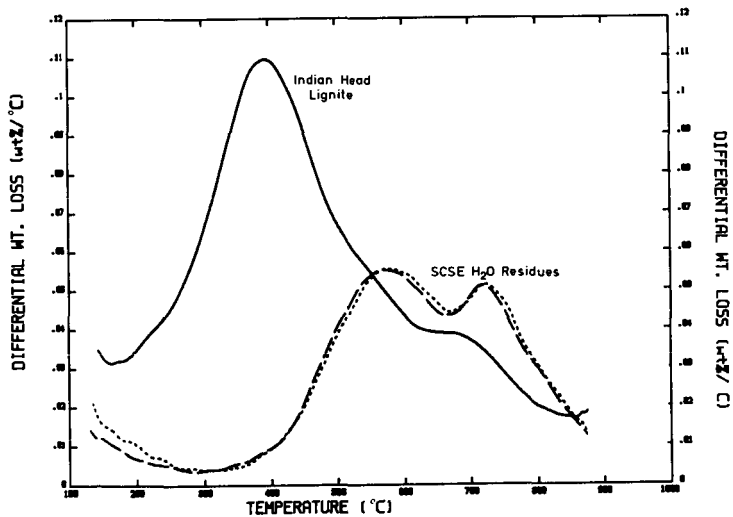


Figure 4. Differential weight loss curves for two supercritical water residues and the original coal.

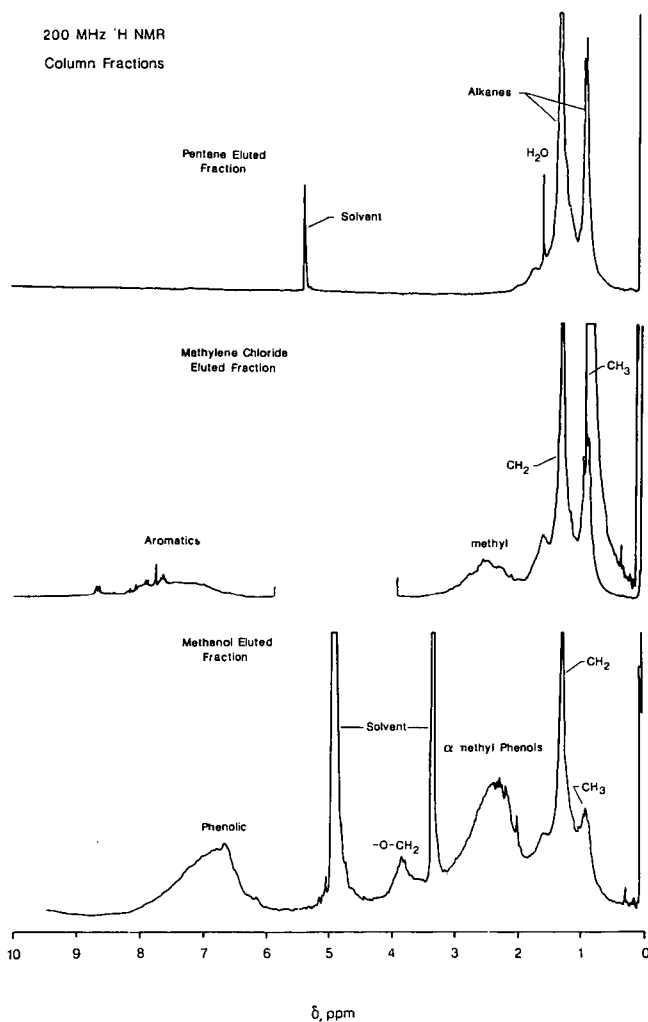


Figure 5. 200 MHz proton NMR of three fractions of a supercritical water extract obtained at 380°C and 3265 psia.